Randomly Branched Bisphenol A Polycarbonates. I. Molecular Weight Distribution Modeling, Interfacial Synthesis, and Characterization

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ABSTRACT: Randomly branched bisphenol A polycarbonates (PCs) were prepared by interfacial polymerization methods to explore the limits of gel-free compositions available by the adjustment of various composition and process variables. A molecular weight distribution (MWD) model was devised to predict the MWD, G, and weight-average molecular weight per arm (M_w/arm) values based on the composition variables. The amounts of the monomer, branching agent, and chain terminator must be adjusted such that the weight-average functionality of the phenolic monomers (F_{OH}) was less than 2 to preclude gel formation in both the long- and short-chain branched (SCB) PCs. Several series of SCB and long-chain branched PCs were prepared, and those lacking gels showed molecular weights measured by gel permeation chromatography–UV and gel permeation chromatography–LS consistent with model calculations. In SCB PCs, the minimum M_w/arm that could be realized without gel formation depended on both composition (molecular weight, terminator type) and process (terminator addition point, coupling catalyst) variables. The minimum M_w/arm achieved in the low molecular weight series studied ranged from ~3300 to ~1000. The use of long chain alkyl phenol terminators gave branched PCs with lower glass-transition temperatures but a higher gel-free minimum M_w/arm. SCB PCs where M_w/arm was less than ~M_c spontaneously cracked after compression molding, a result attributed to their lack of polymer chain entanglements. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 560–570, 2000

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INTRODUCTION

Branching is a well-known structural modification of polymers done primarily for the alteration of their rheological properties.[1] Branching of step-growth polymers usually is achieved by incorporation of a monomer with a functionality (f) greater than 2. Such polymers are called *randomly branched* because of the statistical distribution of the branched segments in the polymer. To avoid crosslinking at complete monomer conversion, monofunctional chain terminators must be used in conjunction with the multifunctional monomers such that the weight-average functionality (F) of the monomers satisfies eq 1, where $w_{i,j}$

and $f_{i,j}$ are the weight fraction and functionality of i monomers having j reactive groups, respectively. Similar relationships are established for less than complete conversions.[2] Key assumptions for these relations include equal reactivity for similar functional groups and all molecular weights and the absence of intramolecular reactions:

$$F_j = \sum w_{i,j} f_{i,j} \leq 2 \tag{1}$$

Random branching is technologically important in several step-growth polymers, particularly poly(ethylene terephthalate)[3] (PET) and bisphenol A (BA) polycarbonates[4] (PCs). In both of these classes of commercial polymers, branched versions are manufactured for their greater degrees of melt strength and shear-rate sensitivity. Very low degrees of branching typically are required to achieve these effects. Highly branched PCs have been prepared from cyclic oligomers[5] and trisphenol derivatives,[6] but these polymers require special monomers, reaction conditions, or both. The numerous references to randomly branched polycondensates and processes for their preparation (e.g., refs. 3 and 4) typically utilize ≤2 mol % branching agent to produce thereby only long-chain branching. No systematic study has appeared on the synthesis and structure–property relationships of randomly branched step-growth polymers in general, or PCs in particular, that takes into consideration the scope and limitations of the applicability of eq 1.
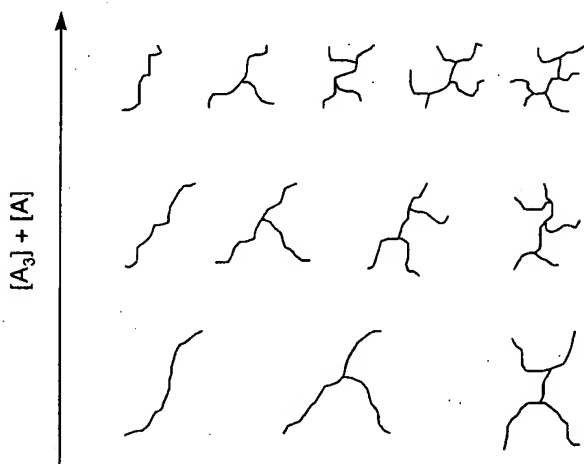

Figure 1. Structure–composition trends for randomly branched condensation polymers.
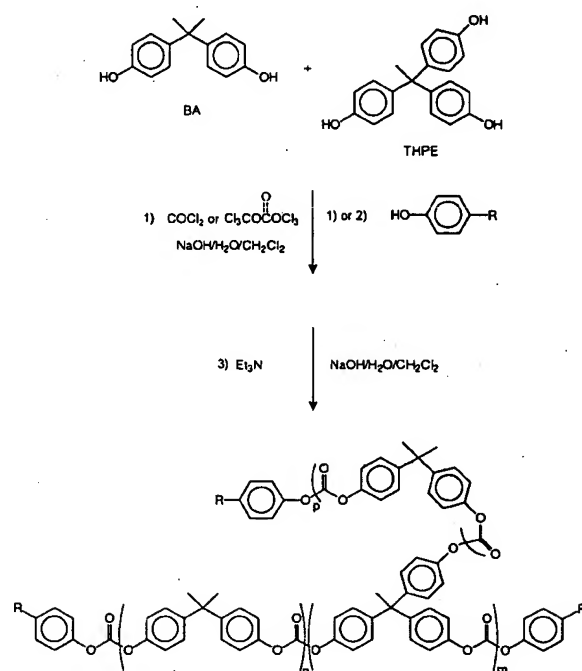

Figure 2. Interfacial synthesis of THPE randomly branched PCs.

The effects on the structure of randomly branched polycondensates by the limits imposed by F_j follow the trends illustrated in Figure 1. The use of a monofunctional chain terminator to preclude crosslinking and the polydispersity effect cause the maximum-number fraction of branched chains to be 0.25,[1] so for any amount of trifunctional branching agent A_3 and chain terminator A_1, the major component of such a randomly branched polymer is, in fact, linear. As the relative amounts of A_3 and A_1 are increased, the number-average branches/chain increases, and the average lengths of the linear chains and branch segments—which can be quantified as the weight-average molecular weight per arm (M_w/arm)—of the resulting mixtures decrease. Those polymers with an M_w/arm greater than the critical molecular weight for entanglements (M_c, from measurements of bulk viscosity vs M_w) can be called *long-chain randomly branched*. The commercial randomly branched versions of PET and PC are such mixtures. Related polycondensates with an M_w/arm less than the M_c can be considered *short-chain randomly branched*. One of the objectives of this study was to explore the properties, particularly the melt rheology, of randomly branched polymers as their M_w/arm decreased below the M_c toward the entanglement molecular

weight ($M_e \sim 0.5\ M_c$, from shear modulus measurements). In the extreme, short-chain randomly branched polymers might have properties similar to those of hyperbranched polymers and dendrimers, such as low melt viscosities for their molecular weight.[7] An important aspect not illustrated in Figure 1 is the polydispersity of each equally branched component, which increases with the degree of branching.

The design of several series of randomly branched step-growth PCs with systematically varying M_w's and M_w/arm values of interest in this study required the development of a molecular weight distribution (MWD) model. Such a model was devised by the modification of a previously developed method for linear step-growth polymers.[8]

This article describes the MWD modeling, the applicability of the monomer functionality limit, the synthesis of polymers with a broad range of M_w/arm values, and the preliminary characterization of branched PCs as an illustrative step-growth polymer. Details presented include the limits of the branched PCs that were prepared without formation of a crosslinked polymer and the interfacial process variables that affected those limits.

EXPERIMENTAL

Chemicals

BA (Dow Chemical Co., Midland, MI; PARABIS™ grade), dichloromethane (J. T. Baker, Phillipsburg, NJ; Baker grade) 50 wt % sodium hydroxide (caustic; J. T. Baker), triethylamine (TEA; Aldrich Chemical Co., Milwaukee, WI), 4-dimethylaminopyridine (DMAP; Aldrich Chemical Co.), phosgene (5-lb cylinders from Matheson Co., Parisippany, NJ), triphosgene (98%; Aldrich Chemical Co.), tris(4-hydroxyphenyl)ethane (THPE; Hoechst Celanese Corp., Frankfurt, Germany), octadecylphenol (ODP; Schenectady International, Schenectady, NY), 3-pentadecylphenol (PDP; 90%; Aldrich Chemical Co.), 1 N hydrochloric acid (J. T. Baker), p-tert-butylphenol (PTBP; Aldrich Chemical Co.), tetrahydrofuran (THF; J. T. Baker), and deionized water (from a Millipore, Bedford, MA, Milli-RX 45 water purification system) were used as received.

Analytical

Liquid chromatography (LC) and gel permeation chromatography (GPC) were done on a Hewlett–Packard (Palo Alto, CA) Model 1090 system connected to a UV diode array detector. Reversed-phase LC analyses were done with a Chromsep HPLC Column SS (Varian Corp., Walnut Creek, CA) (150 mm × 4.6 mm) containing Spherisorb ODS 2 (3 μm).[9] GPC-UV analyses were done with two Polymer Labs (Amherst, MA) gel-mixed B columns (10 μm, 7 mm × 30 cm) and THF at 1 mL/min calibrated with a single, broad molecular weight BA PC standard (M_w = 29,850; M_n = 12,700). Sample solutions in CH_2Cl_2 (0.25 wt %) contained ~200 ppm of a toluene flow marker (~18-min retention time).

The absolute molecular weight and branching determinations were performed by GPC in combination with a light-scattering detector (GPC-LS). Sample solutions of 100 to 150 mg in 50 mL of CH_2Cl_2 were filtered through a 0.5-μm Millipore Millex-LCR filter and transferred to a Shimadzu (Columbia, MD) SIL-9A autosampler. Separation was achieved via three Polymer Labs PL-gel 10-μm mixed B columns with THF as the mobile phase at 35°C and a flow rate of 1 mL/min with a Perkin–Elmer (Oak Ridge, TN) 200 LC pump. An injection volume of 50 μL was employed. Eluting polymer concentrations were measured with a Waters (Milford, MA) 410 differential refractometer (DRI), and light-scattering intensities at three angles (45°, 90°, 135°) were measured via a miniDawn tri-angle laser-light-scattering (TRALLS) detector from Wyatt Technology Corp. (Santa Barbara, CA). The total run time was 30 min. After a delay of 10 min, the DRI and TRALLS were collected during 20 min with a sampling rate of 2/s. Data were recorded and reduced with Astra software (Version 4.20, Wyatt Technology Corp.) and Microsoft (Redmond, WA) Excel for Windows 95. The molecular moments were calculated from the weight fraction and molecular weights at each retention time (absolute method) and from the weight fraction via the linear reference.

Differential scanning calorimetry (DSC) was performed with a DSC 2910 differential scanning calorimeter from Du Pont Instruments (New Castle, DE). The polymer was heated at 20 °C/min under N_2. The glass-transition temperature (T_g) was reported as the half height of the heat-flow curve. The decomposition temperatures (T_d's) were determined by thermogravimetric analysis with a TGA 2950 from Du Pont Instruments. The T_d was the temperature at which 5% of the sample was lost by heating under nitrogen at 20 °C/min.

Table I. Reactants for 100-mL-Scale Branched PC Syntheses

	m/m BA		g	
Entry	PTBP	THPE	PTBP	THPE
a	0.020	0.002	0.026	0.005
b	0.040	0.004	0.052	0.011
c	0.044	0.005	0.057	0.013
d	0.047	0.041	0.061	0.108
e	0.083	0.022	0.107	0.058
f	0.083	0.030	0.107	0.079
g	0.083	0.035	0.107	0.092
h	0.083	0.040	0.107	0.105
i	0.083	0.045	0.107	0.118

The presence of gels was determined qualitatively by the passage of 3 mL of the polymer solution in CH_2Cl_2 through a 0.5-μm filter. Plugging of the filter indicated the presence of the gelled polymer.

MWD Calculations

MWD and G values were calculated with the spreadsheet version of the model written in Microsoft Excel for Windows 95 and were run on an IBM P100 personal computer. Values are reported based on a monomer conversion of p = 0.9985. Estimates of M_w for linear PCs with equal GPC elution volumes of the branched PCs were calculated[13] as $M_{w,l} = M_w(G)^{k/(1+a)}$, where k = 1.4 and a = 0.695 as estimated from the dilute solution viscometry. M_w/arm values were calculated with the Fortran version of the model written in VMS and run on a Digital Equipment Corp. VAX mainframe. Maxima of 13 branches/chain and 300 monomer segments/chain, with the above p, were used.

100-mL-Scale Synthesis of the Branched PCs (Entry a, Table I)

To a 500-mL Erlenmeyer flask was added 1.96 g of BA (8.58 mmol), 0.005 g of THPE (0.017 mmol), 50 g of water, 1.4 g of 50% NaOH (17.1 mmol), and a stirring magnet. To the magnetically stirred mixture was added 3 g of phosgene (11 mmol) in 30 mL of CH_2Cl_2, and stirring was continued for 5 min. Then, 1.25 g of 50 % NaOH (15.6 mmol) was added, and the mixture was stirred for 5 min. A solution of 0.026 g of PTBP (0.172 mmol) in 10 mL

of CH_2Cl_2 was added, and the mixture was stirred for an additional 5 min. Then, 0.20 mL of 5% aqueous TEA was added, and the mixture was stirred for 15 min to complete the polymerization. Finally, ~1 g of phosgene in 10 mL of CH_2Cl_2 was added to reduce the pH to ~9. The mixture was added into a separatory funnel, and the aqueous phase was removed. The organic phase was washed once with ~0.5 volumes of 1 N HCl and then to neutral with water. The branched PC was recovered by addition to hot water[9] and was dried under vacuum at 100 °C with an N_2 flow. Other branched PCs were made by this method with the amounts of THPE and PTBP shown in Table I. Molar amounts of the branching agent and terminator relative to BA are indicated as mol/mol or m/m.

1-L-Scale Synthesis of Branched PCs (Entry b, Table II)

Reactions were carried out in a 1-L resin flask fitted as previously described,[9] except that a phosgene-gas inlet tube was not used. Triphosgene was added with a solid addition funnel connected to a low-torque motor. A glass rod standing on the auger of the addition funnel and a vibrator aided in the feeding of triphosgene through the funnel. The reactor was placed in an ice bath supported by a lab jack.

After the reaction flask was purged with N_2, 460 mL of water was added and purged again; then, 68.5 g (0.30 mol) of BA, 0.367 g (0.0012 mol) of THPE, 280 mL of CH_2Cl_2, and 48 g of NaOH (to pH 12.5) were added with stirring at ~300 rpm. The pH electrode tip was placed near the top of the aqueous (upper) phase. The mixture was agitated at ~500 rpm so that the mixture was emulsified fully. The temperature of the reactor was maintained at about 20 °C by the addition of water and dry ice to the ice bath. Before the inlet tube of the NaOH was placed on the reactor, the air was purged out of the line and the NaOH pump controller was adjusted to 20% of the maximum rate. Then, 37 g of triphosgene (0.127 mol) was weighed into a beaker and crushed with a glass rod to reduce the particle size to about a 1-mm diameter. The N_2 reactor purge was stopped, and triphosgene was poured into the addition funnel. A glass rod was placed in the addition funnel to aid in the feeding of triphosgene. The spatula and beaker were rinsed with aqueous NH_3 to neutralize residual triphosgene. Triphosgene was added to the reactor at about 1.5 g/min

Table II. Reactants for 1-L-Scale Branched PC Syntheses

Sample	PTBP (g)	THPE (g)	PDP (g)	ODP (g)	Triphosgene (g)
1a	1.17	0.37			37
1b	1.81	0.37			37
1c	2.21	0.82			37
1d	2.12	1.01			37
1e	3.60	2.02			37
1f	6.31	3.86			37
1g	14.20	9.09			37
1h	43.70	28.92			37
2d	2.12	1.01			37
2f	6.31	3.86			40
2g	14.20	9.09			40
3e	4.73	2.02			40
3f	7.65	3.86			50
3g	15.77	9.18			55
3h	45.97	28.92			60
4d(I)		1.01		4.88	37
4d(II)		1.01		4.88	37
4f(II)		3.86		14.53	37
5d(I)		1.01	4.77		37
6e(II)	4.73	2.02			40
7e(I)		2.02	10.66		44
7e(II)		2.02	10.66		44
7f(II)		3.86	17.06		44

at about 20 °C with stirring at 500 rpm. Then 1.80 g (0.012 mol) of PTBP was added, and the mixture was stirred for 5 min before 290 mL of CH_2Cl_2 was added. Then, 0.44 mL (0.003 mol) of TEA was added, and the agitator was increased to 800 rpm. NaOH was added as needed to maintain a pH greater than or equal to 12. After 30 min of stirring, the polymerization was complete, and the pH was reduced to ~9 by the addition of ~3 g of triphosgene via a spatula. The stirrer was turned off to allow phase separation, after which the upper, aqueous layer was removed with suction. 100 mL of 1 N HCl was added to the organic phase and was stirred for 5 min. Water then was added to fill the reactor, and the mixture was stirred for 5 min. The phases were allowed to separate, and the aqueous phase was removed. Water washing was repeated until the water remained at pH 5 to 7. The reaction mixture alternatively could be divided into two parts and washed with water as described previously if the phase separation was slow. The branched PC was recovered as described previously and dried at 80 to 100 °C (at least 20 °C below the estimated T_g). Variations in the amounts and types of reactants used by this method are summarized in Table II.

RESULTS AND DISCUSSION

MWD Model

M_w and M_n were calculated with the formulae given by Roovers.[1] Stockmayer's theory [10,11] was used to calculate the detailed MWD (i.e., to calculate $M_{w,i}$ and w_i, which were used in the subsequent equations). The calculation procedure was similar to the monofunctional case detailed by Munjal[8] and the tetrafunctional monomer case described by Nakamura.[12] The constraints for the combination of a monofunctional terminator and a trifunctional branching agent are shown in Tables III and IV.

The G parameter is defined as the ratio of the square of gyration for the branched polymer chain

Table III. Constraints on the n_i and m_i Values[8] for Zero Branches per Chain (AA, BB Monomers)

Group No.	m_1	m_2	m_3	n_2
1	0	i	0	$i - 1$ to $i + 1$
2	1	i	0	i to $i + 1$
3	2	i	0	$i + 1$

versus the linear polymer chain of the same true molecular weight. This parameter was derived by Rudin[13] in terms of the average number of branches per chain. To properly calculate G, one would have to compute the complete MWD. However, this becomes difficult for the case of high degrees of branching because of computation requirements. Therefore, the following correlation was developed after it was observed that G is essentially a function of the trifunctional/terminator mole ratio: $G = 0.992 - 0.38097 \, Y - 2.37352 \, Y^2$, where Y represents the moles of the branching agent per mole of the terminator.

The M_w/arm plays a key role in the structure–property relationships of randomly branched polymers. This term is defined by eq 2, where i is the number of branches per molecule, $M_{w,i}$ is the M_w of the molecules with i branches per chain, and w_i is the weight fraction of the molecules with i branches per chain:

$$M_w/\text{arm} = \frac{\sum_{i=1}^{N_{max}} (M_{w,i}/(2*i + 1))*w_i}{\sum_{i=1}^{N_{max}} w_i} \quad (2)$$

Sensitivity to F with the 100-mL-Scale Synthesis Method

The applicability of F to define the limits of gel-free branched PCs prepared by interfacial polymerization (Fig. 2) was investigated with a small-scale synthetic method. Conditions were employed to give a relatively dilute (4 wt %) polymer solution so that the eventual molecular weight would not be limited by solution viscosity. Because in this and the larger scale interfacial PC synthesis method the excess of (tri)phosgene used was hydrolyzed, only the phenolic (OH) groups required consideration in the monomer functionality calculation. The amounts of BA, THPE, and PTBP were adjusted systematically to give a

Table IV. Constraints on the n_i and m_i Values for k Branches per Chain for the Trifunctional Branching Agent

Group No.	m_1	m_2	m_3	n_2
1	0	i	k	$i + k - 1$ to $i + 2*k + 1$
2	1	i	k	$i + k$ to $i + 2*k + 1$
3	2	i	k	$i + k + 1$ to $i + 2*k + 1$
⋮	⋮	⋮	⋮	⋮
$k + 3$	$k+2$	i	k	$i + 2*k + 1$

Table V. GPC-UV Analysis of 100-mL-Scale Branched PC

Entry	F_{OH}	GPC-UV		
		M_w	M_n	Disp.
a	1.991	46,120	15,190	3.0
b	1.977	30,380	11,000	2.8
c	1.981	28,950	11,780	2.5
d	2.020	Gelled		
e	1.979	39,420	6,540	6.0
f	1.988	57,160	9,910	5.8
g	1.993	89,760	10,140	8.9
h	1.998	160,790	8,630	18.6
i	2.003	Gelled		

range of weight-average functionality (F_{OH}) values of 1.977 to 2.020 (Table V). Both of the compositions in which F_{OH} was greater than 2 gelled (Entries d and i), whereas those with lesser values, even as high as 1.998 (Entry h), did not. Although the gels could not be isolated, their presence in the polymer solutions was observed readily by the plugging of filters and emulsification of the reaction mixture. The MWD of these polymers as measured by GPC-UV showed increasing M_w's and polydispersities (disp.), as expected, with increasing branching agent (Entries e–h).

Composition Limits and Process Variations with the 1-L-Scale Synthesis Method

A wide range of branched PCs were prepared on a larger scale to investigate how certain composition and process variables affect the ability to prepare gel-free polymers and to determine some of the properties of the resultant products. Triphosgene, which reacts as 3 mol of phosgene when introduced to the PC reaction mixture, was used in these larger scale preparations. MWD calculations were done beforehand to generate target compositions with systematic structural variations such that within each series the polymers had about the same M_w but a decreasing M_w/arm value (Table VI). The variations considered in these preparations included terminator amount and type (PTBP, ODP, or PDP), terminator addition point (post or prior to triphosgene addition), coupling catalyst (TEA or DMAP), and molecular weight (relatively high or low). The key aspects of each series are summarized by the following:

Table VI.   Target MWDs and Branching Parameters of Branched PCs

Entry	Terminator	Model Calculations ($p = 0.9985$)				
		M_w	M_n	G	$M_{w,1}$	M_w/arm
1a	PTBP	60,400	20,770	0.88	54,200	15,050
1b		33,160	13,430	0.93	31,200	11,750
1c		41,690	12,360	0.84	36,200	7,970
1d		61,510	13,650	0.77	49,700	7,480
1e		63,240	9,080	0.71	47,500	4,280
1f		66,330	5,870	0.66	47,300	2,490
1g		61,190	3,220	0.64	42,200	1,250
1h		66,290	1,720	0.62	44,500	590
2d		61,510	13,650	0.77	49,700	7,480
2f		66,330	5,870	0.66	47,300	2,490
2g		61,190	3,220	0.64	42,200	1,250
3e		25,820	6,540	0.81	21,600	3,320
3f		25,480	4,670	0.75	20,100	2,030
3g		25,040	2,840	0.69	18,400	1,050
3h		25,590	1,620	0.65	17,900	510
4d(I)	ODP	61,510	13,650	0.77	49,700	7,480
4d(II)		61,510	13,650	0.77	49,700	7,480
4f(II)		66,330	5,870	0.66	47,300	2,490
5d	PDP	61,510	13,650	0.77	49,700	7,480
6e	PTBP	25,820	6,540	0.81	21,600	3,320
7e(I)	PDP	25,820	6,540	0.81	21,600	3,320
7e(II)		25,820	6,540	0.81	21,600	3,320
7f(II)		25,480	4,670	0.75	20,100	2,030

Series 1. Post PTBP addition, high M_w.
Series 2. Prior PTBP addition, high M_w.
Series 3. Prior PTBP addition, low M_w.
Series 4. Post (I) or prior (II) ODP addition, high M_w.
Series 5. Post PDP addition, high M_w.
Series 6. Prior PTBP addition, DMAP catalyst, low M_w.
Series 7. Post (I) or prior (II) PDP addition, DMAP catalyst, low M_w.

The first three targets were designed to achieve a branched PC similar to current commercial resins (1b) and two variations therefrom, with a higher molecular weight ($M_w \sim 60,000$) branched PC having the same amount of branching agent (1a) and with a branched PC having an M_w close to that of 1a but about twice the amount of branching agent (1c). These three targets are each long-chain branched based on the aforementioned criteria. For the other samples, the amounts of terminator and branching agent were adjusted to obtain targets within each series with about the same M_w with a decreasing M_w/arm value. The M_w targets for the high molecular weight series

were about 62,000 and for the low molecular weight series were about 25,000. The high molecular weight target was chosen to improve the chances of compression-molding the samples without spontaneous cracking, whereas the low molecular weight target was just above that of the lowest molecular weight linear PCs considered durable.[4] Calculated G values decrease as expected with increasing amounts of branching agent. M_w/arm values were targeted to be above and below the M_c of linear BA PC ($M_c = 5500$ daltons)[14] and below the M_c to a minimum of $\sim$500 daltons. The last condition is only possible for the low molecular weight series. *Each of these target compositions has an F_{OH} of less than 2 and, therefore, should not form gels under ideal polymerization conditions.*

Samples 1a to d had no gels but higher than expected M_w's, with 1a and 1c being significantly higher (Table VII). This result could have arisen from degrees of monomer conversion higher than that used in the model. The other series show that the ability to prepare gel-free short-chain branched (SCB) PCs depended on both the type of terminator used and the process conditions em-

Table VII. Analyses of Branched PCs

| Sample | Model $M_{w,1}$ | Gel | GPC-UV | | | Oligomer wt % | T_g (°C) | T_d (°C) |
			M_w	M_n	Disp.			
1a	54,200	No	75,900	22,300	3.4	2.6	153	469
1b	31,200	No	39,100	15,240	2.6	3.5	149	444
1c	36,200	No	51,000	15,300	3.3	2.9	147	461
1d	49,700	No	56,550	15,740	3.6	3.0	148	465
1e	47,500	No	42,960	10,500	4.1	6.4	142	464
1f	47,500	Yes	42,530	10,390	4.1	17.0	127	449
1g	42,200	Yes	26,000	4,050	6.4	28.0	113	395
1h	44,500	Yes	17,060	2,600	6.6	43.0	78	254
2d	49,700	No	51,600	16,500	3.1	2.2	149	476
2f	47,300	No	34,360	8,490	4.1	12.0	134	460
2g	42,200	Yes	26,530	5,580	4.8	26.0	117	417
3e	21,600	No	21,300	7,900	2.2	11.0	137	455
3f	20,100	No	16,300	5,820	2.8	18.0	129	439
3g	18,400	No	18,400	4,940	3.7	33.0	111	415
3h	17,900	Yes	11,190	2,860	3.9	42.0	85	311
4d(I)	49,700	No	37,800	15,000	2.5	6.0	125	440
4d(II)	49,700	No	40,900	16,100	2.5	7.0	125	421
4f(II)	47,300	Yes						
5d(I)	49,700	No	38,800	13,000	3.0	8.0	121	420
6e	21,600	No	23,100	8,200	2.8	11.0	140	465
7e(I)	21,600	No	21,000	7,700	2.7	12.0	92	432
7e(II)	21,600	No	40,700	9,500	4.3	10.0	97	435
7f(II)	20,100	Yes						

ployed. The gel-free minimum M_w/arm for series 1 (post PTBP addition, high M_w) was just under the M_c at ~4200 daltons. The samples containing gel had lower than expected M_w's because of the fractionation of the crosslinked component. Polydispersity and multimodality increased as expected with increasing degrees of branching, as illustrated by the chromatograms for series 3 (Fig. 3). The more highly branched PC samples tended to show lower than predicted M_w's. It is likely that the highly branched fractions collapsed in volume similar to hyperbranched polymers and dendrimers,[7] and, therefore, the GPC-UV result was not corrected fully with G alone. Adding PTBP prior to triphosgene allowed the preparation of gel-free sample **2f** with an M_w/arm value just below the M_e (at ~2500 daltons). A disadvantage of adding the terminator earlier is the increase in % oligomers. Using more PTBP in lower molecular weight series 3 extended the gel-free minimum M_w/arm value to well below the M_e (to ~1000 daltons; sample **3g**).

LC analysis shows the types, distribution, and total amount of low molecular weight oligomers present in these PCs,[15] as illustrated in the chromatograms for series 3 (Fig. 4). The wt % of the oligomers is defined as the fraction eluting prior to 37.2 min, the retention time at which a broad polymer peak begins to elute. The result corresponds to those species with a molecular weight of up to ~3500. PC oligomers primarily are composed of terminator-capped linear (L_n) and cyclic (C_n) species, where the subscript refers to the number of BA carbonate repeat units present. The oligomer pattern of these branched PCs was generally the same as that observed for linear PCs; no major THPE-based or other peaks were resolved under the LC conditions used. As illustrated in the chromatograms, the total amount and distribution of cyclic oligomers remained relatively constant with increasing degrees of branching, but the linear oligomers increased with increasing PTBP concentration.

These results show clear limits to the minimum M_w/arm value for gel-free SCB PCs made from BA, THPE, and PTBP with this interfacial polymerization method. The use of the more organic-soluble DMAP coupling catalyst gave the same MWD as the standard TEA catalyst (compare **3e** and **6e**). Although the formation of cyclic

oligomers and low molecular weight linear oligomers certainly affected the MWD and effective monomer concentrations, we believe that the major cause of gel formation in the SCB PCs was minor differences in the overall relative monomer reaction rates, which could be modulated significantly by phase-distribution effects, under interfacial conditions. If so, then the limits described here would not be observed under noninterfacial conditions, such as in solution or melt polymerization.[4]

The use of chain terminators bearing long chain alkyl groups provided large T_g decreases in hyperbranched polyesters,[16] and this approach was explored in randomly branched PCs with ODP and PDP. The samples in series **4** that used ODP all gave lower than predicted molecular weights. The linear oligomers in the long chain alkyl phenol terminated PCs were shifted to much longer retention times because of their lower water solubility. Therefore, the % oligomers for these samples were determined from those
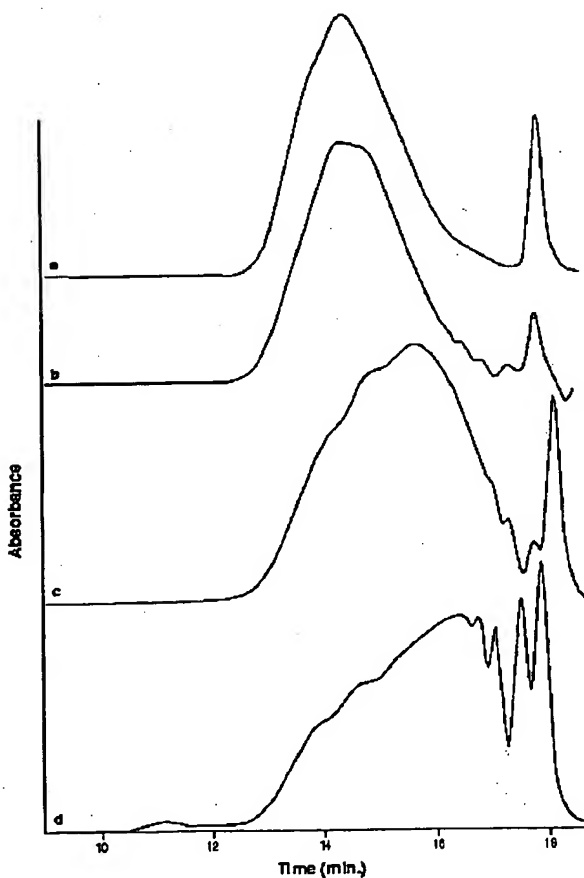

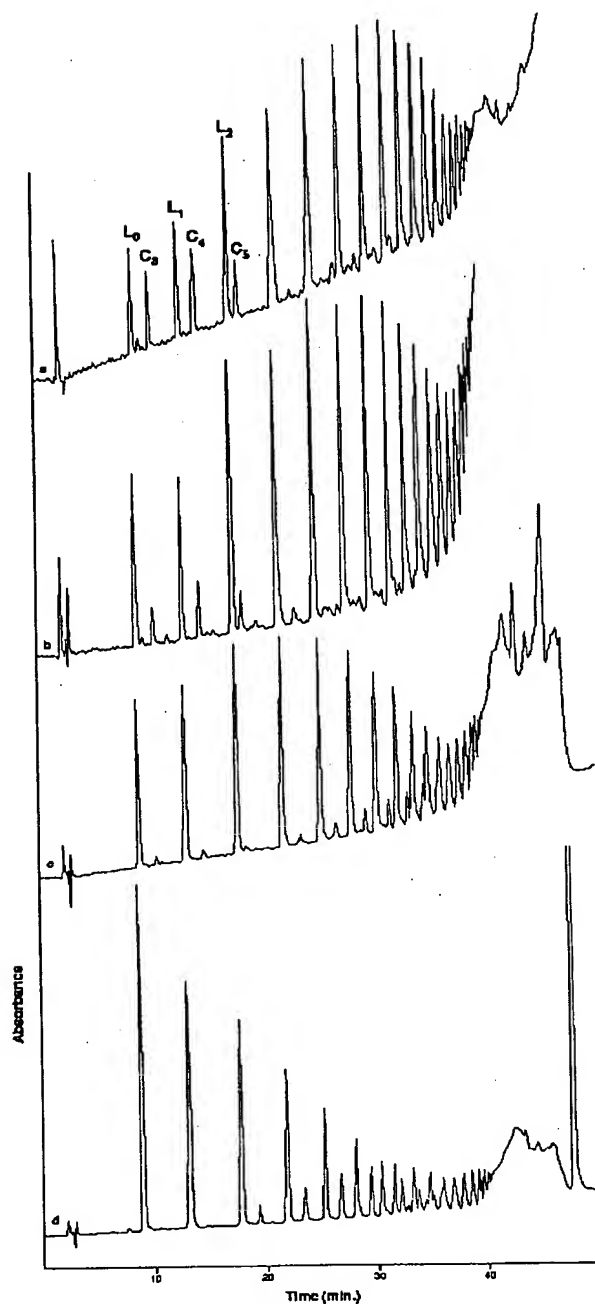**Figure 3.** GPC-UV of **3e–h** (a–d, respectively).

Figure 4. LC of **3e–h** (a–d, respectively).

oligomers eluting up to ~42 min. The T_g's for these PCs were reduced in proportion to the amount of terminator and the length of the alkyl chain. Complications in the reactivity of ODP were suspected because of the presence of *ortho-* and *para-*isomers. To remove this uncertainty, PDP, which is exclusively the *meta-*isomer, was used in subsequent experiments. Sample **5d(I)**